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Reactivity of Organic Substances in Atmospheric Photooxidation Reactions

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
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REACTIVITY OF ORGANIC SUBSTANCES IN ATMOSPHERIC PHOTOOXIDATION REACTIONS

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ABSTRACT

The organic vapors emitted to urban atmospheres by motor vehicles and other sources of emissions consist not only of paraffinic, acetylenic, aromatic, and olefinic hydrocarbons, but also of aldehydes, ketones, alcohols, phenols, and chlorinated hydrocarbons. To estimate the contribution of each of these classes of compounds to photochemical smog, one must know both their atmospheric concentrations and their relative reactivities in atmospheric reactions.

A review of the available literature on concentration levels of organic vapors in urban atmospheres indicates that much more analytical work is needed. The existing data are adequate, however, for the formulation of useful estimates.

Reactivities of organic substances in photooxidation reactions can be considered from many standpoints. Rates of disappearance of the organic substances, rates of disappearance of nitric oxide or of formation and disappearance of nitrogen dioxide, and rates or maximum yields of various products such as oxidant or organic nitrates all can be used as chemical measurements of reactivity. Eye irritation, various types of plant damage, and aerosol formation are indicators of reactivity that can be related only to a limited extent to chemical measurements of reactivity. The problems of developing a single index of reactivity are considered.

The application of reactivity measurements to automobile exhaust composition, to control devices, and to improvements in atmospheric purity is discussed.

REACTIVITY OF ORGANIC SUBSTANCES IN ATMOSPHERIC PHOTOOXIDATION REACTIONS

"Photochemical reactivity," or "reactivity," may be defined as the tendency of an atmospheric system containing organic substances and nitrogen oxides to undergo, under the influence of ultraviolet radiation and appropriate meteorological conditions, a series of chemical reactions that result in the various manifestations associated with the photochemical type of air pollution. These manifestations include eye irritation, plant damage, and visibility reduction. Although this type of air pollution has been associated with the Los Angeles basin, it is also experienced elsewhere in California and in many other urban areas in the United States. The constant increase in the use of petroleum products in motor vehicles and in other combustion sources could result in photochemical air pollution becoming a problem throughout the world in urban centers that are characterized by unfavorable meteorological conditions.

The chemical reactions are initiated by the photochemical dissociation of nitrogen dioxide by solar radiation below 4000 A. Subsequent chemical reactions result in the rapid conversion of nitric oxide to nitrogen dioxide, usually followed by a nitrogen dioxide maximum and the further reaction of nitrogen dioxide. After nitrogen dioxide reaches a maximum concentration, oxidant, including particularly ozone and peroxyacyl nitrates, begins to form. Aerosol also is produced. Aldehydes and organic nitrates are the predominant organic substances known to be produced by these reactions. Included in the products are the substances responsible for eye irritation and for several types of plant damage. The aerosol formed causes visibility reduction.

On the basis of the available literature, it is not clear whether one or several "measures" of reactivity are necessary to define the atmospheric system. Measures include the rate of reaction of the various participating organic reactants, the rate of oxidant formation, and the degree of eye irritation. The characterization of these measures of reactivity certainly is not an academic exercise. The most economical and effective methods of control of photochemical "smog" depend on decisions as to the most desirable modifications of the atmosphere. It is essential to keep in mind that a control device is not an end in itself, but merely a means of modifying an urban atmosphere. To understand what may be accomplished by an air pollution control device, its potential effect on the reactivity of the atmosphere also must be understood. The reactivities obtained for various classes of compounds can be combined with detailed analytical data on emissions to determine the effectiveness of various engine exhaust systems or fuel modifications.

The reactivity of photochemical smog can be evaluated by using experimental data on the following:

1. Rates of disappearance of organic substances from irradiated single organic substance — nitrogen oxide mixtures, from multi-component organic substance -- nitrogen oxide mixtures, and from auto exhaust mixtures.
2. Ability of organic substances to participate in the photochemically induced conversion of nitric oxide to nitrogen dioxide.
3. Rate of formation or yield of ozone or oxidant.
4. Rates of formation or yields of aldehydes and peroxyacyl nitrates.
5. Aerosol formation.
6. Plant damage.
7. Eye irritation.

The rates of disappearance of individual hydrocarbons and some of the other organic substances can be obtained irrespective of the complexity of the mixture. In general, however, direct association of the experimental results obtained in *(2)* through *(7)* with individual organic reactants in the mixture is not possible. Exceptions would be limited to comparisons or results involving two- or at most three-component organic substance — nitrogen oxide mixtures with results involving the corresponding single-component systems. Even in such comparisons as these, assumptions about additivity of effects have rarely been verified experimentally. Complex interactions may well occur in all of those effects that are strongly dependent on the ratio of hydrocarbon to nitrogen oxide as well as on hydrocarbon type and concentration.

The available experimental data cannot be used except after critical evaluation. For example, as reported by different investigators, the data on aldehydes and ketones produced from irradiation of single hydrocarbon — nitrogen oxide systems sometimes include large differences in yields. Differences of 50 to 100 percent in the yields reported are not uncommon for certain aldehydes or ketones.

It must be decided whether comparisons are to be made at those ratios of reactants giving maximum effects irrespective of the possible differences in these reactant ratios for various systems. Effects certainly cannot be assumed *a priori* to maximize at the same ratio for different single- or multi-component organic substance — nitrogen oxide systems.

Irrespective of the limitations cited and others that could be discussed, it is important to attempt to make judgements on the parameters that affect the reactivity of photochemical atmospheres. At the same time, the assumptions made and the criteria for selection of data should be explicitly stated so that the results may be modified conveniently.

CHEMICAL MEASURES OF REACTIVITY

Chemical measures of reactivity include the rates of disappearance of reactants and the rates of formation or the yields of various products. Great care must be exercised in equating such chemical measures with the effects of more direct concern, namely, eye irritation, plant damage, and visibility reduction. In this study these chemical measures of reactivity are used to define differences in the reactivity of classes of organic substances. The chemical measures of reactivity are not used to assign precise contributions to photochemical air pollution from each of a large number of individual organic substances. This latter approach requires more accurate and detailed chemical and biological experimental results than presently exist or are likely to exist in the near future.

It appears doubtful that a single summed measure of biological reactivity can be defined for individual substances. Eye irritation, the various types of plant damage, and aerosol formation are not necessarily caused by the same substances nor are these effects necessarily associated with the same reaction mechanisms. It is not meaningful to combine yields of products such as ozone, aldehydes, and peroxyacyl nitrates and define the result as an overall measure of reactivity. Such an exercise ignores multiple effects of some of the products and interaction effects. The association of either total reactivity or a single measure such as eye irritation with a given set of chemical species ignores the distinct possibility that unidentified species exist which cause biological effects. This approach also is dependent on the sensitivity of yields of some products to concentration and ratio of reactants.

These comments certainly are not meant as an argument against chemical reactivity studies or the even more desirable combinations of chemical and biological investigations. It is essential, however, that the difficulties in the reactivity approach be recognized and that great caution be taken in interpreting results and arriving at general conclusions.

Reactions of Organic Substances

Rates of reaction or times for partial consumption of various hydrocarbons and aldehydes have been reported in a number of studies (Table 1,2, and 3). These investigations include both laboratory measurements on irradiations of individual organic substances with nitrogen oxides in air and irradiations of diluted auto exhaust *(1-7)*. The measurements have been made both in static reactors and in stirred dynamic flow reactors. Irradiations involve the use of combinations of fluorescent lamps and sometimes mercury arcs to simulate solar radiation in the ultraviolet region. The measurements of the disappearance of the organic substances in static irradiations have been reported as follows: *(1)* times to half-conversion to products,

(2) percentage of substances converted per hour, and *(3)* normalized "rate constants" for the most rapidly changing portion of the experimental concentration versus time curves. In dynamic irradiations, measurements are given as the percentage of the substance consumed near dynamic equilibrium during a given average irradiation time *(5-7)*.

TABLE 1. RANKING OF REACTIVITIES OF HYDROCARBONS WHEN PHOTOOXIDIZED IN PRESENCE OF NITROGEN OXIDES UNDER STATIC CONDITIONS

Hydrocarbon	Ranking of hydrocarbons		
	Schuck and Doyle [a]	Stephens and Scott [b]	Tuesday [c]
Tetramethylethylene	10	10	10
Trans-2-butene	6		8
Cis-3-hexene		6	
Isobutene	1.5	2	2
1,3-Butadiene	1		
Propylene	1	2	1
m-Xylene		1	
p-Xylene	0.5	0.5	
Ethylene	0.1	0.3	
Hexanes, Octanes	< 0.1		
Pentanes	< 0.01		

[a] Reference 1. [b] Reference 2. [c] Reference 3.

TABLE 2. RANKING OF REACTIVITIES OF AROMATIC HYDROCARBONS WHEN PHOTOOXIDIZED IN PRESENCE OF NITROGEN OXIDES UNDER STATIC CONDITIONS

Aromatic hydrocarbon	Ranking of reactivities [a,b]
1,2,3,5-Tetramethylbenzene	10
1,2,5-Trimethylbenzene	8
1,2,4-Trimethylbenzene	6
1,2,3-Trimethylbenzene	6
m-Xylene, 3-methylethylbenzene	3
o-Xylene	1.5
p-Xylene, p-diethylbenzene	1.5
Toluene, ethylbenzene, isopropylbenzene	1
Benzene	0.5

[a] Based on percent consumed in first hour of reaction.
[b] Reference 4.

TABLE 3. RANKING OF REACTIVITIES OF ORGANIC SUBSTANCES WHEN PHOTOOXIDIZED IN PRESENCE OF NITROGEN OXIDES UNDER DYNAMIC CONDITIONS.

	Auto exhaust studies		"Pure component" studies
Organic substances	Sigsby et al.[a]	Leach et al.[b]	Klosterman et al.[c]
2-Alkenes	10	d	
Trans-2-butene			9
1,3,5-Trimethylbenzene		6	8
1,3-Butadiene	7		8
1-Butenes, 1-pentenes	7	d	7
Propylene	5	6	
1,2,4-Trimethylbenzene		6	
Xylenes	3	4	5
Formaldehyde			5
Propionaldehyde			4
Ethylene	1	3	3
Toluene	1	2	2
Pentanes	0.5		
Butanes		0.5	
Cyclohexane			0
Isooctane			0
Benzene		0	
Acetylene		0	
Ethane		0	

Based on percent hydrocarbon consumed near dynamic equilibrium:

[a] Reference 5.

[b] Reference 6.

[c] Reference 7.

[d] 85% of all butenes and pentenes reacted.

The most reactive organic substance measured in each study involving static irradiations has been arbitrarily rated as 10, and the other substances rated relative to 10 on the basis of the experimental data available (Table 1 and 2). Data from the dynamic irradiation work have been treated differently. The experimental data from these studies have been rated on the following basis: 0 percent conversion, 0; 0 to 5 percent conversion, 0.5; 5 to 15 percent conversion, 1; 85 to 95 percent conversion, 9; and above 95 percent conversion, 10 (Table 3).

Since the experimental measures of rate are not the same in these investigations, the rating scales are not completely compatible with each other. The numerical values for a given substance cannot be expected to be identical in the various investigations. Furthermore, different concentrations of reactants, light intensities, and temperatures were used, and rates of reaction do not necessarily change proportionately with these differences in experimental conditions.

Despite all of these limitations, the rankings of sub-classes of organic substances and of many of the individual compounds are very con-

sistent. Branched or straight-chain olefins with internal double bonds, e.g. tetramethylethylene or trans-2-butene, form the most reactive subclass. The trialkylbenzenes, the tetraalkylbenzenes, and olefins with terminal double bonds (except ethylene) rank next, followed by the dialkylbenzenes, aldehydes, and ethylene. Toluene is less reactive than ethylene, and the paraffinic hydrocarbons, acetylene, and benzene are less reactive than toluene.

The least reactive hydrocarbons are consumed so slowly in the photooxidation reactions that accurate experimental measurements are difficult to obtain. Variations of flow in dynamic flow irradiations and adsorption losses and leaks in static and dynamic experiments could account for some of the small, but non-zero rates reported in some studies. The whole body of experimental evidence indicates that most paraffinic hydrocarbons, acetylene, and benzene react at rates at least 2 orders of magnitude less than the most reactive substances. In the laboratory the substances rated at 10 are half-consumed in the order of 0.1 hour, whereas the least reactive substances should require 10 to 100 hours for half-conversion to products. Some substantiation of the upper end of this time scale is given by the report that no loss of acetylene or ethane could be detected after an 18-hour irradiation of an atmospheric sample *(2)*.

Irradiations of polluted air masses by sunlight occur for from 8 to more than 14 hours a day, depending on season and latitude *(8)*. Peak intensities vary by about a factor of 3, and 50 percent of peak intensity is exceeded from 5 to 10 hours a day, again depending on season and latitude. Thus the irradiation period of practical interest is about 10 hours. If the air mass should not be dispersed, the same air mass may be irradiated for more than 1 day. On the basis of such considerations, it matters little within a large metropolitan area whether a component reacts appreciably in 0.1, 1, or even several hours. Ultimately, the effects of its reaction products may be felt somewhere in the area in terms of eye irritation, plant damage, or visibility reduction. Thus any substance that can be largely consumed during the daylight hours should be considered potentially undesirable. On the other hand, substances such as most of the paraffinic hydrocarbons present in significant concentrations, acetylene, and benzene, which do not appear to react appreciably during this time period, cannot contribute significant amounts of products.

The reaction of the organic substance is necessary but not sufficient evidence that an adverse biological effect could be associated with the photooxidation of that substance. Although a substance reacts, it does not follow *a priori* that it produces significant amounts of eye irritants, phytotoxicants, or oxidants or that it will participate in reducing visibility. Product yields and biological effects also must be

measured if any generally meaningful evaluation of reactivities is to be obtained.

Photooxidation of Nitric Oxide to Nitrogen Dioxide in Presence of Hydrocarbons.

The ability of a wide variety of hydrocarbons to participate in the conversion of nitric oxide to nitrogen dioxide has been determined in one study *(9)*. The ranking of the hydrocarbons used in these static irradiations is shown in Table 4. The ranking follows the same general order as that obtained from rates of hydrocarbon disappearance. Although this measure of reactivity is no better fundamentally than that based on hydrocarbon reaction, it does have the advantage of simplicity in analytical measurement. Measurement of the hydrocarbons requires either gas chromatography with several column substrates or an infrared instrument with a long-path cell. The nitrogen dioxide formation rate can be determined by manual measurement of nitrogen dioxide or with a monitoring instrument.

TABLE 4. REACTIVITIES OF HYDROCARBONS BASED ON ABILITY TO PARTICIPATE IN PHOTOOXIDATION OF NITRIC OXIDE TO NITROGEN DIOXIDE [a]

Hydrocarbon	Ranking
Trans-2-butene	10
1,2,5-Trimethylbutene	6
Isobutene	6
m-Xylene	5
Propylene	5
1,2,3,5-Tetramethylbenzene	5
1,3-Methylethylbenzene	3
1,2,4-Trimethylbenzene	3
o-Xylene, p-Xylene	2
Ethylene	2
o- and p-Diethylbenzene	1.5
Propylbenzenes	1.5
Toluene, ethylbenzene	1
Benzene	0.5
n-Nonane	0.5
3-Methylheptane	0.25
Acetylene	0.25
Methylpentanes	0

[a] Reference 9.

Reaction of Nitrogen Dioxide to Products

Data also are available on the rate of conversion of nitrogen dioxide to products in the presence of various hydrocarbons *(9)*. The per-

centage of total nitrogen oxides reacted was related to hydrocarbon and nitrogen oxide concentration and ratio in a study of irradiated auto exhaust under dynamic conditions *(10)*. The percentage-reacted curves versus initial concentrations of hydrocarbons and nitrogen oxides resembled the oxidant curves versus the reactant concentrations. Furthermore, when the percentage of nitrogen oxide reacted was zero, the oxidant level was also zero. Percentage of nitrogen dioxide reacted also followed the same trend as did the plant damage effects, with little or no nitrogen dioxide converted or plant damage observed at low ratios of hydrocarbon to nitrogen oxide. Again, this index can be readily obtained by a nitrogen dioxide analysis.

Oxidant Yields

The term 'oxidant' refers to that group of substances formed in the photochemical type of air pollution that are capable of oxidizing potassium iodide and other chemical reagents. These oxidants include ozone, nitrogen dioxide, peroxyacyl nitrates, possibly other types of organic peroxy compounds or radicals, and atomic oxygen. Because the relative responses of the various oxidant methods or instruments to these substances vary, the concentrations of oxidant reported by different procedures should not necessarily agree. Ozone, the major constituent of the oxidant, is a phytotoxicant; it also causes rubber cracking. There is some evidence that respiratory distress is caused by atmospheric levels of ozone. Eye irritation has been suggested as being statistically, but not causatively, associated with moderate to high atmospheric oxidant levels.

Several methods that are claimed to be relatively specific for ozone have been proposed. Two of these methods, one based on rubber cracking and the other on infrared absorption, have been used to obtain measurements of the ozone formed during the irradiation of a large number of organic substance — nitrogen oxide mixtures in air *(1,11)* (Table 5).

Rubber cracking measured as cracking depth in millimeters has been used to determine ozone produced by irradiating a wide variety of hydrocarbons, aldehydes, alcohols, ketones, acids, and organic nitrogen compounds with nitrogen dioxide *(11)*. Measurements of total ozone exposure of the rubber strips were made during a 10-hour irradiation of 3 ppm of the organic substance and 2 ppm of nitrogen oxide at 30° to 33°C and 30 percent realative humidity.

Cracking depths of more than 5 millimeters were observed when olefins with an internal double bond, a diolefin, dialkylbenzenes, a trialkylbenzene, higher-molecular-weight alcohols, butyric acid, biacetyl, and alkyl nitrites were irradiated with nitrogen dioxide. Cracking depths of 3 to 5 millimeters were observed when olefins with a terminal double bond (except ethylene), aldehydes, methanol, ethanol, and propionic acid were irradiated along with nitrogen dioxide. Ethylene

TABLE 5. OZONE OR OXIDANT YIELDS FROM PHOTOOXIDATION OF ORGANIC SUBSTANCE — NITROGEN OXIDE MIXTURES.

		Static irradiations		Dynamic irradiations
Organic Substance	Haagen-Smit Cracking depth, mm [a]	Schuck and Doyle ppm by volume [b]	Altshuller and Cohen ppm by volume [c]	Klosterman et al., ppm by volume [c]
1,3-Butadiene	12	0.65		0.72
2-Alkenes	8	0.55 - 0.73		
1,3,5-Trimethylbenzene	7		1.1	0.37
Xylenes	6-7	0.18	0.65 - 1.0	
1-Alkenes	5	0.58 - 1.00		0.4
Methanol, ethanol	5			
Formaldehyde	4			1.05
Propionaldehyde	4		1.0	0.80
3-Methylheptane	3			
n-Nonane	3		0.2	
Ethylene	2	1.1		0.69
Hexanes, heptanes	1	~0.2		0.0
Toluene	0.6		0.5	0.36
Acetylene	0.5		0.0	
c_1 - c_5 Paraffins	< 0.2	0.0 - 0.2		

[a] Reference 11. [b] Reference 1. [c] Reference 9. Reference 7.

and most six-carbon and higher paraffinic hydrocarbons caused 1 to 3 millimeters of cracking depth when irradiated with nitrogen dioxide. Irradiation of acetylene — nitrogen dioxide mixtures caused only 0.5 millimeter of cracking depth. Very little or no cracking of the rubber strips was observed when methane, ethane, propane, butanes, pentanes, formic acid, or acetic acid were irradiated with nitrogen dioxide in air.

The infrared measurements of ozone in the work reported by Schuck and Doyle were essentially instantaneous compared to the rubber-cracking measurements *(1)*. Data were obtained on the ozone produced by irradiating a wide variety of olefins and paraffinic hydrocarbons along with a few other types of compounds at concentrations of 3 or 6 ppm with 1 or 2 ppm of either nitric oxide or nitrogen dioxide. The ozone concentrations reported were the equilibrium values.

From 0.38 to 1.1 ppm of ozone was formed during irradiation of the various olefins with nitrogen oxides *(1)*. The ozone yields from the terminal double-bonded monoolefin — nitrogen oxide irradiations overlapped those from the internally double-bonded monoolefin — nitrogen oxide irradiations. This result is not in agreement with that obtained by rubber-cracking measurements, which indicated that more ozone was produced by irradiating internally doublebonded monoolefins with nitrogen oxides. Similarly, irradiation of ethylene with nitrogen oxide produced the highest ozone concentration reported in this latter study, whereas irradiated ethylene — nitrogen dioxide mixtures caused less rubber cracking than that produced from other olefin — nitrogen dioxide mixtures. The xylene used in the study reported by Schuck and Doyle was presumably p-xylene; when irradiated with nitrogen oxide, this xylene participated in the formation of only 0.18 ppm of ozone. Although p-xylene was not used in the rubber-cracking measurements, m-xylene and o-xylene were used; when irradiated with nitrogen dioxide, these aromatic hydrocarbons participated in the formation of as much ozone as was produced by irradiation of olefin — nitrogen dioxide mixtures.

Irradiation of several five- and eight-carbon paraffinic hydrocarbons with the nitrogen oxides resulted in the production of only 0.15 to 0.26 ppm of ozone. When methane, methylethylketone, trichloroethylene, and tetrachloroethylene were irradiated with nitrogen oxides, very little or no ozone was detected *(1)*. These results appear to be in general agreement with the small or undetectable amounts of rubber cracking observed in the irradiation of similar systems.

In a later study *(9)* oxidant measured colorimetrically by the potassium iodide method was determined after irradiation of a number of different aromatic hydrocarbon — nitric oxide systems, aldehyde — nitric oxide systems, and several others (Table 5). Oxidant con-

centrations from 0.65 to 1.1 ppm were produced when p-xylene, o-xylene, m-xylene, and 1,3,5-trimethylbenzene were irradiated with nitric oxide. Toluene — nitric oxide mixtures produced 0.5 ppm of oxidant when irradiated. The oxidant yields from the irradiation of acetylene — nitric oxide, n-nonane — nitric oxide, and propionaldehyde — nitric oxide mixtures were 0.0, 0.2, and 1.0 ppm, respectively.

A recent investigation *(7)* with both static and dynamic reaction conditions confirms the fact that aromatic hydrocarbons (except benzene) and several of the aliphatic aldehydes, when irradiated with nitrogen oxides, produce oxidant concentrations within the same range as those measured in irradiated olefin — nitrogen oxide mixtures (Table 5). Under dynamic flow conditions no oxidant was detected during the irradiation of four paraffinic hydrocarbons containing six or eight carbon atoms.

The results discussed above indicate that olefins, aromatic hydrocarbons, and aldehydes all should contribute to atmospheric ozone and oxidant levels. The ability of higher-molecular-weight paraffinic hydrocarbons to participate in oxidant formation under static conditions is on the average only about a third to a fifth that of the aromatic hydrocarbons, olefins, or aldehydes. The overall reactivity of the six-carbon and larger paraffins with respect to oxidant formation also appears to be small because no oxidant was detected when these hydrocarbons were irradiated with nitrogen oxides under dynamic conditions. The one- through five-carbon paraffins have no tendency or only a very slight tendency to participate in oxidant formation, even in static experiments.

Aldehydes

Some investigators attribute much of the eye irritation effects observed to the presence of formaldehyde and acrolein in polluted atmospheres *(1)*. Plant damage also has been caused by irradiation of certain aldehydes *(7, 12)*. Although some of the atmospheric aldehydes come directly from combustion sources, photooxidation reactions probably contribute a large portion of these aldehydes.

Formaldehyde is produced by the photooxidation of almost all olefins and aromatic hydrocarbons in the presence of nitrogen oxides *(1, 7, 9)*. Photooxidation of some of the higher aldehydes also could contribute some formaldehyde *(7)*. Other aliphatic aldehydes, i.e., acetaldehyde, propanal, butanal, acrolein, and others are largely formed from olefin — nitrogen oxide reactions *(1)*. The photooxidation of higher-molecular-weight aldehydes produces aldehydes with smaller numbers of carbon atoms *(7)*. Although aromatic hydrocarbons (except benzene) produce formaldehyde when irradiated with nitrogen oxides, there is no evidence that acetaldehyde, propanal, or other such aliphatic aldehydes exist

as reaction products. *(7,9)*. Analyses for total aldehydes do indicate the presence of aldehydes other than formaldehyde (*7,9*). Analyses for dicarbonyl compounds indicate the formation of molecules with two carbonyl groups as products from the photooxidation of aromatic hydrocarbons with nitrogen oxides *(9)*. Thus, it appears that the aldehyde yields from aromatic hydrocarbons consist of formaldehyde along with aldehydes containing two aldehydic groups.

Molar yields of formaldehyde based on initial olefin concentrations usually are in the 0.3 to 0.5 range (Table 6). Molar yields of formaldehyde based on initial dialkyl or trialkylbenzene concentrations range from 0.15 to 0.2. On the basis of these results, it may be expected for equal concentrations of the two classes of hydrocarbons that the yield of formaldehyde from aromatics should be about half that from olefins.

Molar yields of aliphatic aldehydes cover a wider range than do those of formaldehyde (Table 6). Molar yields from aliphatic aldehydes

TABLE 6. ALDEHYDE YIELDS FROM PHOTOOXIDATION OF HYDROCARBON — NITROGEN OXIDE MIXTURES

	Moles of aldehyde per mole of hydrocarbon [a]		
Hydrocarbon	Formaldehyde	Acrolein	Aliphatic Aldehydes
Ethylene	0.3 - 0.4		0.3 - 0.4
Propylene	0.4		0.6 - 0.8
1-Butene	0.4		0.65
Isobutene	0.5 - 0.7		0.5 - 0.7
Trans-2-butene	0.35		1.25 - 1.55
1,3-Butadiene	0.3 - 0.5	0.2 - 0.3	0.5 - 0.8
1-Pentane	0.5		1.0
2-Methyl-2-butene	0.3 - 0.5		0.8 - 1.2
Cis-2-hexene			0.9 - 1.0
Toluene	.05		.1
Xylenes	0.15 - 0.2		0.2 - 0.3
1,3,5-Trimethylbenzene	0.15 - 0.2		0.3 - 0.4

[a] Based on hydrocarbon initially present as reactant.

also are more uncertain because of the limitations in the measurements. The yields reported from aromatic hydrocarbons may be too low because the analytical method used does not respond well to dicarbonyl compounds.

Very little or no formaldehyde or other aldehydes are detected in the irradiation of any paraffinic hydrocarbon — nitrogen oxide system. Similarly, no formaldehyde is detected as a product when nitrogen oxides are irradiated in the presence of methylethyl ketone, trichloroethylene, or tetrachlorethylene.

Ketones

Ketones such as acetone and methylethyl ketone are formed from the photooxidation of olefins such as isobutene, 2-methyl-2-butene, and other branched-chain olefins *(1)*. Acetone and methylethyl ketone show little photochemical reactivity *(1,9,11)*, and at present there is no evidence that they cause any direct biological effect.

Peroxyacyl Nitrate Yields

The members of the peroxyacyl nitrate series have been shown to cause plant damage and eye irritation *(12)*. Peroxyacyl nitrate yields from irradiation of a number of olefins and aromatic hydrocarbons with nitrogen oxide at 5 ppm of a reactant have been reported *(2-4)*. Peroxyacyl nitrate yields from 0.55 to 1.0 ppm were formed from the irradiation of propylene, several butenes, and hexenes with nitric oxide or nitrogen dioxide. No peroxyacyl nitrate was formed from ethylene. The internally double-bonded olefins when irradiated with nitrogen oxides produced more peroxyacyl nitrates than did the olefins with terminal double bonds. The xylenes, 1,2,4,5-tetramethylbenzene, and 1,3,5-trimethylbenzene reacted in the presence of nitrogen oxides to form 0.4 to 0.8 ppm of peroxyacyl nitrates.

The peroxyacyl nitrate yields from four irradiated olefin — nitrogen oxide systems were studied as a function of initial nitrogen oxide concentration. The yields depended on whether nitric oxide or nitrogen dioxide was used as the reactant. The maximum yield did not occur at the same ratio of reactants from system to system. The maximum yields from the tetramethylethylene and trans-2-butene — nitrogen dioxide systems were about twice those from the propylene or isobutene — nitrogen dioxide systems. The effect of variations of initial nitrogen oxide concentration on peroxyacyl nitrate closely resembled the behavior observed for ozone or oxidant.

The peroxyacyl nitrates were observed as products from irradiation of propionaldehyde — nitrogen oxide mixtures *(7)*. Irradiations of C_4 to C_5 paraffins, n-hexane, 3-methylpentane, 2,3-dimethylbutane, cyclohexane, and isooctane with nitrogen oxides did not produce peroxyacyl nitrates in detectable yields *(1,2,7)*. Very small yields (0.02 to 0.05) of peroxyacyl nitrates were reported from the irradiation of 2-methylheptane and 2-methylpentane with nitrogen oxide *(1)*.

Aerosol Formation as a Measure of Reactivity

Visibility reduction caused by atmospheric aerosols is one of the characteristics of the photochemical type of air pollution. It is well known that particulate matter in the proper size range can effectively penetrate the respiratory tract. A synergistic effect has been demonstrated with respect to certain respiratory function tests when some gases are adsorbed on particulates. There does not appear to be clear proof, however, that adverse respiratory effects are caused by aerosols formed in photochemical reactions Eye irritation effects are not increased when photochemically produced aerosols are present *(13)*.

Olefins of five or fewer carbon atoms when irradiated in the presence of nitrogen dioxide form very little aerosol *(1, 14)* (Table 7). The corresponding olefin — nitrogen dioxide — sulfur dioxide mixtures form large

TABLE 7. EFFECT OF SULFUR DIOXIDE ON AEROSOL FORMATION IN NITROGEN DIOXIDE — HYDROCARBON REACTIONS [a]

Hydrocarbon	Photometer reading [b]	
	Olefin, NO_2	Olefin, $NO_2 - SO_2$
Ethylene	0.1	2.2
1-Butene	0.05	2.85
2-Butene	0.05	3.0
1-Pentene	0.1	3.05
2-Pentene	0.0	3.0
1-Hexene	0.05	3.35
2-Hexene	0.25	3.05
3-Heptene	0.45	3.35
2,4,4-Trimethyl-l-pentene	3.3	3.3
n-Butane		0.1
2-Methylpentene		0.0

[a] Reference 14.

[b] Readings before irradiation were subtracted from readings during irradiation. Reactant concentration, ppm: olefin, 10; NO , 5; SO , 2.

amounts of aerosol upon irradiation *(1, 14)*. The irradiated ethylene — nitrogen dioxide — sulfur dioxide mixture produces much less aerosol than do mixtures containing the other olefins. Olefins with internal double bonds do not appear to participate in the formation of any more aerosol than is formed by irradiating olefins with terminal double bonds with nitrogen dioxide and sulfur dioxide. The aerosol in all of these systems at appreciable relative humitities is sulfuric acid aerosol *(15, 16)*. Six-carbon and higher-molecular-weight olefins when irradiated with nitrogen dioxide can form aerosol, but a large increase

in aerosol occurs when sulfur dioxide is added to most of these systems *(17)*.

Aromatic hydrocarbon — nitrogen dioxide mixtures when irradiated in the absence of sulfur dioxide can produce aerosol *(7,17)*. Aerosol also is produced by the irradiation of aromatic hydrocarbon — nitrogen dioxide — sulfur dioxide mixtures *(17)*. The quantitative effects of sulfur dioxide on aerosol formation in these systems have not been studied in detail. Intensity appears to be a more critical experimental parameter in the systems containing aromatic hydrocarbons *(16)*.

No aerosol formation has been observed when aldehyde — nitrogen dioxide systems have been irradiated. No data appear to be available on irradiated aldehyde — nitrogen dioxide — sulfur dioxide mixtures. No significant level of aerosols has been reported from the irradiation of either paraffinic hydrocarbon — nitrogen dioxide or paraffinic hydrocarbon — nitrogen dioxide — sulfur dioxide mixtures *(1,14)*.

When irradiated with nitrogen dioxide, reactive organic molecules of higher molecular weight appear capable of forming what must be an organic aerosol. Lower-and higher-molecular-weight olefins and aromatic hydrocarbons both form aerosol when irradiated in the presence of nitrogen dioxide and sulfur dioxide together.

Plant Damage as a Measure of Reactivity

A number of plant-damaging substances are produced by reactants or products of photochemical reactant. Ethylene can cause damage to ornamental plants, cotton, and tomatoes. Ozone and peroxyacyl nitrates also are phytotoxicants for many plant species. The irradiation of most olefin — nitrogen oxide and aromatic hydrocarbon — nitrogen oxide mixtures produces phytotoxicants including ozone and peroxyacyl nitrates. Irradiation of ethylene — nitrogen oxide mixtures has failed to produce plant damage (except damage due to ethylene itself) to tobacco wrapper, pinto bean, petunia, cotton, or endive *(7,18)*. No peroxyacyl nitrate-type compound is formed from this system *(2,7)*. The diolefin 1,3-butadiene also failed to produce damage to tobacco wrapper, pinto bean, or petunia *(7)*. Other types of olefins when irradiated with nitrogen oxide do produce phytotoxicants.

Damage to tobacco wrapper, pinto bean, and petunia is produced by irradiated 1,3,5-trimethylbenzene — nitrogen oxide mixtures *(7)*. Other of the more reactive aromatic hydrocarbons that produce appreciable yields of peroxyacyl nitrates also should cause plant damage.

Olefin — ozone mixtures that contain olefins with five carbon atoms or more and particularly those that can give four-carbon or larger fragments produce a short-lived phytotoxicant that causes damage to pinto bean and tobacco *(12)*. This phytotoxicant apparently is not

responsible for most types of plant damage termed typical oxidant damage. This type of damage is more similar to that caused by peroxyacyl nitrate alone or to that produced by irradiating olefin or aromatic hydrocarbon mixtures.

Irradiation of propionaldehyde and higher saturated aldehydes alone *(7,12)* and in the presence of nitrogen oxides *(7)* causes damage to tobacco wrapper, pinto bean, and petunia similar to that caused by irradiating olefin — nitrogen oxide mixtures. Formaldehyde and acetaldehyde do not cause significant plant damage when irradiated in air *(7,12)*. Formaldehyde — nitrogen oxide mixtures also do not produce a phytotoxicant *(7)*.

In a study of the relative plant-damaging potential of four hydrocarbons irradiated with nitrogen oxide, the severity of damage to pinto bean was in the following descending order: cis-2-butene, propylene 1-hexene, isopropylbenzene *(12)*. In another investigation moderate plant damage by irradiated propylene — nitrogen oxide mixtures was investigated in detail *(18)*. In the same investigation no plant damage was observed from irradiated ethylene — nitrogen oxide or acetylene — nitrogen oxide mixtures *(18)*.

Recently, the plant-damage indices were determined for ethylene, 1-butene, 1,3-butadiene, toluene, 1,3,5-trimethylbenzene, formaldehyde, propionaldehyde, n-hexane, 3-methylpentane, 2,4,4-trimethylpentane, and cyclohexane *(7)*. On the basis of data from irradiations of 2 to 3 ppm of organic substance with nitrogen oxide, the severity of damage to pinto bean and petunia was as follows: 1,3,5-trimethylbenzene, severe; propionaldehyde, severe; 1-butene, moderate to severe; all other hydrocarbons, none.

The results discussed above are summarized in Table 8. If the damage to young pinto bean and petunia is largely due to peroxyacyl nitrates, then substances that form high yields of peroxyacyl nitrates, such as 2-butene, 1-butene, and mesitylene, should cause moderate to severe damage and substances that form little or no peroxyacyl nitrates, such as ethylene, 1,3-butadiene, formaldehyde, acetylene, toluene, and paraffinic hydrocarbons, should not cause any appreciable damage.

The degree of damage to pinto bean and petunia has been shown to be sensitive to reactant ratio in a study of irradiated auto exhaust under dynamic flow conditions (Table 9). When the ratio of hydrocarbon (carbon ppm) to nitrogen oxide was 3:1 and sometimes 6:1, no plant damage was observed. Under these experimental conditions, no oxidant was produced in the irradiated mixtures and the conversion of nitrogen dioxide to products that would include the peroxyacyl nitrates was minimal. Consequently, the measurements of product formation indicate, as they should, that little or none of the phytotoxi-

TABLE 8. PLANT DAMAGE FROM IRRADIATED ORGANIC SUBSTANCE — NITROGEN OXIDE MIXTURES

Substance	Severity of plant damage to pinto bean or Petunia [a]
2-Butene	severe
1,3,5-Trimethylbenzene	severe
Propionaldehyde	severe
1-Butene	moderate to severe
Propylene	moderate
1-Hexene	moderate
Isopropylbenzene	light
Ethylene	none
Toluene	none
Formaldehyde	none
Acetylene	none
Hexanes	none
Isooctane	none

[a] References 7 and 12.

TABLE 9. PLANT INJURY INDEX [a,b]

Young pinto bean: lower-surface glazing-type injury

	NO_x, ppm			
	1/4	1/2	1	2
0			0	
3	0.4	0.1	0	0
6		2.0	1.0	0
12		3.0	3.5	0

Petunia: total injury (all phytotoxicants)

	NO_x, ppm			
	1/4	1/2	1	2
0			0	
3	1.1	1.2	0	0
6		2.6	1.3	0
12		2.0	3.0	0

[a] Note: Index based on scale of 0 to 4; 4 = maximum damage.

[b] Reference 10.

cants that have been identified are present when there is no plant damage.

Irradiation of mixtures containing either about 0.5 ppm of ethylene, 1-butene, and trans-2-butene or 0.5 ppm of the xylenes with 1 ppm of nitrogen oxides does not produce significant plant damage *(7)*. When mixtures containing 0.5 ppm of both the xylenes and the olefins with 1 ppm of nitrogen oxides (twice the hydrocarbon to nitrogen oxide ratio) are irradiated, moderate damage is experienced by pinto bean and petunia. Thus, the presence of both aromatic hydrocarbons and olefins in the irradiated mixtures is necessary to reproduce the plant damage results in irradiated auto exhaust.

Eye Irritation as a Measure of Reactivity

Eye irritation as it occurs in areas exposed to the photochemical type of air pollution is an aggravating effect. No definite clinical condition has been associated with this effect. Irritation of the nose and throat also can occur. Laboratory measurements in recent years have been confined to obtaining the subjective response of human panelists to irritation of their eyes by various mixtures. Time to initial irritation or intensity of irritation is reported by each panelist. The results are averaged and reported as a single time in seconds or minutes or as a number on an intensity scale.

Eye irritation responses reported in two studies are shown in Tables 10 and 11 *(1,10)*. Additional work has been done elsewhere *(19)*. The available results show that ethylene participates in forming smaller amounts of eye irritating substances than do other olefins and that 1,3-butadiene and other diolefins form larger amounts of irritating substances than do monoolefins. The more limited data on aromatic hydrocarbons and aldehydes indicate that upon irradiation with nitrogen oxides these classes of substances form as much irritant material as do all but the most reactive olefins. Irradiation of hexanes or octanes at 3 ppm (18 to 24 carbon ppm) with nitrogen oxide produces few or no eye irritants *(1,7)*. Another study of eye irritation from irradiated hexane — nitrogen dioxide mixtures produced no irritation at 5 ppm (30 carbon ppm) of hexane and 2.5 ppm of nitrogen dioxide *(19)*. At 10 ppm and above (60 carbon ppm and above) of hexane and 5 ppm and above of nitrogen dioxide, irritation was experienced after several hours of irradiation of such mixtures. Alcohols and acetylene when irradiated with nitrogen oxide cause very little if any eye irritation *(19)*. The data on chlorinated hydrocarbons and ketones are somewhat conflicting. Although acetone and perchloroethylene have been reported as inactive *(1,19)*, higher-molecular-weight ketones and trichloroethylene have been reported as causing significant eye irritation in one study and no eye irritation in another *(1,19)*.

TABLE 10. COMPARISON OF OBSERVED EYE IRRITATION AND EYE IRRITATION CALCULATED FROM FORMALDEHYDE AND ACROLEIN CONCENTRATIONS [a]

Compound	Concentration ppm	Concentration of NO_x, ppm	Calculated eye irritation [b]	Observed eye irritation [b]
Ethylene	3	1	1.8	2.4
Ethylene	6	2	8.8	8.8
Propylene	3	1	8.0	7.9
1-Butene	3	1	5.6	5.6
Trans-2-butene	3	1	4.0	7.6
2-Methyl-2-butene	3	1	6.0	4.0
1-Pentene	3	1	10.8	14.8
3-Heptene	3	1	9.2	7.6
Cyclohexene	3	1	6.0	8.0
1,3-Butadiene	3	1	3.6	2.4
2-Methyl-l,3-butadiene	3	1	19.9	16.8
Isopentane	9	3	0.8	3.2
n-Pnetane	6	2	0.8	2.8
3-Methylpentane	6	2	0.8	2.4
Methane	6	2	2.0	3.2
2,2,4-Trimethylpentane	3	1	0.8	2.0
Methylethyl ketone	3	1	0.0	1.6
Xylene	3	1	0.8	5.2

[a] Reference 1. [b] Arbitrary Units (24 maximum).

TABLE 11. EYE IRRITATION RESPONSE TO IRRADIATED ORGANIC SUBSTANCE – NITROGEN OXIDE MIXTURE UNDER DYNAMIC CONDITIONS [a]

Organic compound	Concentration, ppm	Concentration of NO_x, ppm	Observed eye irritation index [b]
n-Hexane	2.93	1.1	3
3-Methylpentane	2.92	1.1	0
Cyclohexane	3.45	1.15	0
Isooctane	2.84	1.1	3
Ethylene	3.15	1.0	7
1-Butene	1.11	0.7	7
1-Butene	3.25	0.95	15
1-Butene	4.87	1.0	17
1,3-Butadiene	3.30	.85	22
Tolune	1.93	1.05	10
1,3,5-Trimethylbenzene	0.41	1.1	8
Formaldehyde	6.1	0.9	17
Propionaldehyde	3.5	0.9	10

[a] Reference 7. [b] Based pm 0 to 30 intensity scale.

Irradiation of mixtures containing either about 0.5 ppm of ethylene, 1-butene, and trans-2-butene or 0.5 ppm of the xylenes along with 1 ppm of nitrogen oxide produced only slight eye irritation *(7)*. When mixtures containing both 0.5 ppm of the olefins and 0.5 ppm of xylenes along with 1 ppm of nitrogen oxides were irradiated, moderate eye irritation was experienced. Both the olefin and aromatic hydrocarbon contents of diluted auto exhaust must be present in order to simulate comparable eye irritation effects.

In other measurements on irradiated auto exhaust mixtures, eye irritation was shown to increase with increases in either olefin or aromatic hydrocarbon concentration in the fuel *(19)*. The exhaust from a fuel containing 72 percent aromatics, 8 percent olefin, and 20 percent saturates caused about as much eye irritation when irradiated as was caused by irradiating exhaust from a fuel containing 38 percent aromatics, 23 percent olefins, and 39 percent saturates. When irradiated, exhaust from a high paraffinic fuel caused much less eye irritation.

DISCUSSION

All of the previous discussion has been based on whatever laboratory data were available, irrespective of the concentrations of reactants used. Usually, the concentration of each individual component has been well in excess of the total atmospheric concentration of hydrocarbons on smoggy days. This approach is often necessary in the laboratory to obtain even reasonably reliable experimental results. In the atmosphere the concentrations of these substances may cover at least a 100-fold range from 0.001 to 1 ppm or more (for methane).

It is essential to consider the range of concentrations in polluted atmospheres and the highest reported concentrations of various components. Although a considerable amount of data has been obtained on light hydrocarbons *(20,21)*, only a few measurements are available on higher-molecular-weight aliphatic hydrocarbons and on aromatic hydrocarbons *(20)*. Consequently, the ranges and highest reported values are more uncertain for these substances. The values used are not those obtained immediately adjacent to heavy vehicle traffic. The available measurements of this sort indicate that these concentrations can be several times the values obtained at locations more representative of general area pollution.

The estimated ranges and highest values have been rounded off and are shown in Table 12. These values are only approximate, but are reasonably consistent with total carbon loadings. Higher values than the highest reported to the present are certainly possible. The lower limits in the range are not the lowest values present at times of low pollution and high rates of ventilation. Under these circumstances,

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the concentrations of most individual components would not be detectable analytically and the total concentration of hydrocarbons can be as low as 1.3 to 1.5 ppm.

TABLE 12. ATMOSPHERIC CONCENTRATIONS OF VARIOUS ORGANIC SUBSTANCES

Component	Concentration of organic, ppm by volume	
	Probable normal range in polluted atmosphere	Highest reported value
Methane	2 - 6	7
C_2 - C_5 Paraffins	0.1 - 0.5	0.7
C_6 + Paraffins	0.03 - 0.15	~0.3 - 0.4
Acetylene	0.03 - 0.25	0.3
Ethylene	0.02 - 0.2	0.3
Propylene	0.005 - 0.04	0.05
1-Butene + isobutene	0.002 - 0.01	0.01 - 0.02
2-Butene (cis + trans)	0.001 - 0.005	0.01
1,3-Butadiene	0.001 - 0.005	0.01
1-Pentene	0.001 - 0.005	0.01
2-Pentenes (cis + trans)	0.002 - 0.01	0.01 - 0.02
2-Methyl-1-butene	0.001 - 0.005	0.01 - 0.02
2-Methyl-2-butene	0.002 - 0.01	0.01 - 0.02
C_6 + Olefins	0.01 - 0.05	~0.1 - 0.2
Benzene	0.01 - 0.05	0.07
Toluene	0.01 - 0.06	0.09
Ethylbenzene	0.002 - 0.01	0.01 - 0.02
Xylenes	0.01 - 0.05	0.07
Formaldehyde	0.02 - 0.1	0.2
Acrolein	0.002 - 0.01	0.01 - 0.02

Because of a lack of analytical data on atmospheric concentrations, estimates of the atmospheric levels of nine-carbon and higher aromatic hydrocarbons, most types of oxygenated organic compounds, chlorinated hydrocarbons, and organic nitrates have not been included in Table 12. Rough estimates can be made of the atmospheric concentrations of some of these substances. Auto exhaust and blowby data *(22,23)* indicate that the nine-carbon aromatic hydrocarbons and styrene may be present at concentrations almost equal to that of the three xylenes, which could correspond to atmospheric concentrations as high as 0.05 ppm. The trimethylbenzenes in auto exhaust and blowby are about equal in concentration to m-xylene plus p-xylene, which could correspond to atmospheric concentrations as high as 0.03 ppm. Higher aldehydes appear to about equal formaldehyde in concentration *(6,24)*. Saturated aldehydes of higher molecular weight than acetaldehyde may made up half of the total aldehydes above

formaldehyde. Peroxyacetyl nitrate has been analyzed in some atmospheric samples recently, and concentrations appear to range from a few parts per billion to several hundredths of a part per million in polluted air *(25)*.

The paraffinic hydrocarbons, acetylene, and benzene make up 90 percent or more of the hydrocarbon on the basis of parts per million by volume and 60 to 80 percent on a carbon basis, according to various analyses of urban atmospheres. The methane alone can constitute 70 to 80 percent of the hydrocarbon and one-third to two-thirds of the carbon, even in a highly polluted atmosphere. Thus, much of the hydrocarbon present consists of substances that have been found to be essentially unreactive in laboratory investigations.

The olefins, including ethylene, in the atmosphere probably occur at almost twice the concentration of the aromatic hydrocarbons, excluding benzene. The aldehydes are unique in that they are products of the hydrocarbon — nitrogen oxide reactions and also are capable of reacting further with nitrogen oxide in sunlight. Formaldehyde and acrolein are eye irritants produced in major part by irradiation but also by combustion processes. The photooxidation of acetaldehyde and higher saturated aldehydes results in the formation of more formaldehyde, peroxacylnitrates, and oxidant and thus with prolonged irradiation tends to maintain the biological reactivity of the atmospheric mixture.

If the concentrations on the high end of the probable concentration ranges estimated in Table 12 are used along with the estimates discussed above, the total concentration of these substances at an early morning traffic peak in Los Angeles could be about 7.7 ppm by volume or approximately 13 carbon ppm. These values do correspond to the higher values actually measured. Excluding the paraffins, acetylene, and benzene, this atmospheric mixture contains 0.7 ppm by volume or 4 carbon ppm of olefins, aromatics (except benzene), and aldehydes. This estimate excludes ketones, organic nitrates, chlorinated hydrocarbons, and other possible organic constituents. It is of interest to compare this composition with that in auto exhaust having about the same total carbon loading *(6)*. The auto exhaust mixture, excluding the paraffins, acetylene, and benzene, contained 1.1 ppm by volume or 5.7 carbon ppm of olefins, aromatics (except benzene), and aldehydes. Consequently, for a given total carbon loading, if the same distribution of reactive hydrocarbons is assumed, the irradiated automobile exhaust mixture would be expected to cause high levels of biological effects.

The effects of auto exhaust irradiations on eye irritation and aerosol formation do not appear to be as marked as might be predicted from the relative concentrations of reactive substances in auto exhaust com-

pared to those in the atmosphere. In the laboratory the concentration of organic substances often must be several parts per million before severe eye irritation and greatly reduced visibility occur. Such concentrations are three or four times higher than the maximum atmospheric concentrations *(1,7,12)*. The differences in laboratory and atmospheric responses can be attributed to a variety of factors. These factors include the presence of much lower levels of small particles and condensation nuclei in laboratory mixtures than in the atmosphere, less than adequate analytical data on polluted atmospheres, or artifacts created by laboratory conditions. This latter category would include wall and sampling line losses of particles and active species and the arbitrary use in the laboratory of eye exposures alone rather than eye, nose, and throat exposures, along with differences in the intensity and distribution of light in the laboratory and in the atmosphere.

From the control standpoint it is desirable that olefins and aromatic hydrocarbon levels from vehicle exhausts, evaporation losses, and solvent usage be reduced as much as possible. The reduction of most paraffinic hydrocarbons, acetylene, or benzene appear not to be justified on the basis of reactivity considerations alone. Naturally, there is no reason why these substances should not be reduced along with reactive substances if no additional costs are involved. Since aldehydes also are reactive, hydrocarbons should be converted by control devices to water and carbon dioxide, not to intermediate oxygenated substances.

If either the atmosphere or emission sources are to be monitored routinely for reactive substances, it is obvious that new instrumental approaches for organic substances are essential. Although gas chromatography will provide detailed hydrocarbon analysis, an analysis for one- to eight- or ten- carbon hydrocarbons is involved, time-consuming, and expensive. For certain research projects such detailed measurements are desirable; however, these techniques are difficult to apply to large numbers of routine analyses for extended periods of time.

One approach is to find a way to remove the unreactive substances or conversely to remove the reactive substances and determine them by difference. For atmospheric analyses a method of monitoring methane is of considerable utility, since methane constitutes the greater part of the unreactive material. A method being developed permits such an analysis *(26,27)*. Another procedure involves the removal of unsaturates by use of various chemical adsorbents in a differential determination by flame ionization analysis *(28)*.

A compromise can be made between analysis with an elaborate gas chromatograph and an analysis limited to a flame ionization or nondispersive infrared analyzer. The methane through pentane and acetylene composition can be determined with a single chromatographic

unit. If total carbon is also determined with a flame ionization analyzer, the sum of the lower-molecular-weight hydrocarbons expressed as carbon ppm can be subtracted from the total carbon loading. The difference can be attributed to reactive substances. In atmospheric studies this procedure would exclude almost all of the unreactive substances. In auto exhaust this procedure should subtract much of the unreactive material. Most of the remaining carbon in the essentially unreactive or very slightly reactive substances would be in the hexanes and higher-molecular-weight paraffinic hydrocarbons.

There are many uncertainties in defining the relationship between the chemical, physical, and biological properties of complex atmospheric systems. Much additional research is needed on both the chemical and biological aspects of these systems. It is not feasible to assign a precise measure to each organic substance, but this is not essential for most purposes. If a reasonable background of research data is available on the major classes and sub-classes of organic substances, it is possible to define the problem and recommend the most desirable modifications in atmospheric composition. Certainly, our present knowledge is sufficient to suggest strongly that control measures can be modified from the present gross emission standards to standards based on the chemical, physical, and biological reactivity of the organic substances produced by various sources of emissions. An important need now is to develop techniques and instrumentation that allow monitoring for compliance with such standards for emission sources and also for the atmosphere in a practical and convenient manner.

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